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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): BRL-TR-3069	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: US Army Ballistic Rsch Lab; 6b. OFFICE SYMBOL (If applicable): SLCBR-IB	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code): Aberdeen Proving Ground, MD 21005-5066	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
METHODS FOR EVALUATION OF THERMALLY INDUCED REACTIONS IN LIQUID PROPELLANTS

12. PERSONAL AUTHOR(S)
Klein, Nathan and Leveritt, Charles S.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
TR	FROM Feb 88 TO Oct 88		

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS
FIELD	GROUP	SUB-GROUP	Calorimetry ARC Thermal Stability HAN LGP1845 LGP1846 Hydroxylammonium nitrate TEAN Triethanolammonium nitrate Thermodynamics

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Aqueous mixtures of the nitrate salts of hydroxylamine (HAN) and triethanolamine (TEAN) are homogeneous, ionic solutions that remain liquid over a wide temperature range (<-60°C). They are sufficiently fluidic that they can be pumped rapidly and are being considered for use in medium-to-large caliber guns. The physical and chemical properties of the propellants make them difficult or impossible to study by classical propellant evaluation methods. Thermal stability studies that include the effects of impurities and contaminants require special cognizance because of the unique reactivity of the propellant mixtures.

SEE REVERSE SIDE FOR CONTINUATION

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL: Nathan Klein	22b. TELEPHONE (Include Area Code): (301) 278-6173 / 22c. OFFICE SYMBOL: SLCBR-IB-B

DD Form 1473, JUN 86 *Previous editions are obsolete.*

SECURITY CLASSIFICATION OF THIS PAGE

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19. ABSTRACT (Con't)

Reaction initiation by absorption of thermal energy has been a major experimental method for determination of propellant stability as well as for the study of ignition and combustion phenomena. A modified high-pressure hydrogenation apparatus (AMINCO bomb) has been used for such reaction initiation studies for many years and is now being replaced by an adiabatic calorimeter. The new diagnostic system utilizes a commercially available accelerating rate calorimeter (ARC) that has been modified to make it suitable for use with liquid gun propellants. Safe storage temperatures, as determined with the ARC, are independent of the quantity of material being stored thereby eliminating the extrapolation from small laboratory samples that is a common uncertainty in many stability evaluation test methods.

TECHNICAL REPORT BRL-TR-3069

BRL

METHODS FOR EVALUATION OF THERMALLY INDUCED REACTIONS IN LIQUID PROPELLANTS

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DECEMBER 1989

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I. INTRODUCTION

1. THE PROPELLANTS

Aqueous mixtures of the nitrate salts of hydroxylamine (HAN) and a simple, aliphatic amine (AAN) form a class of gun propellants. The AAN salt that is currently in use is triethanolammonium nitrate (TEAN). These mixtures are colorless, odorless, homogeneous liquids with a very large liquidus range, solidifying to homogeneous glasses at temperatures below -80°C.[1] Although HAN and TEAN each contain both oxidizing and reducing components and thus are individually monopropellants, HAN, NH_3OHNO_3, is too oxidizer-rich and TEAN, $NH(CH_2CH_2OH)_3NO_3$, is too fuel-rich to be used effectively. The HAN and TEAN are mixed in such proportion as to produce N_2, CO_2, H_2O stoichiometry at equilibrium as shown in the following equation:

$$7NH_3OHNO_3 + NH(CH_2CH_2OH)_3NO_3 \text{ ---> } 6CO_2 + 8N_2 + 22H_2O \qquad (1)$$

LGP1845 is formulated on a volumetric basis and is 11.0 molar in total nitrate whereas LGP1846 is gravimetrically formulated to contain 20 % water. The specific compositions of two of the HAN-TEAN propellants is shown in Table 1.

TABLE 1. Propellant Compositions

Propellant	Composition					
	HAN		TEAN		Water	
	(wt. %)	(M)	(wt. %)	(M)	(wt. %)	(M)
LGP1845	(63.23)	9.62	(19.96)	1.38	(16.81	13.64)
LGP1846	60.79	(9.09)	19.19	(1.30)	20.02	(15.93)

The role of water in the formulated propellant is essentially that of solvent and diluent. Thermochemical calculations using the BLAKE code clearly show the effect both of water and HAN:TEAN ratio on impetus.[2] Although maximum impetus is obtained in mixtures that are slightly fuel-rich, the propellants are compounded at N_2, CO_2 stoichiometry in order to reduce the probability of secondary muzzle flash. The effect of water content on impetus is far greater than variation in HAN:TEAN ratio;[3] the effect on a stoichiometric mixture is shown in Figure 1.

As with all chemical systems, the HAN-based propellants are susceptible to thermal degradation. Such degradation can be the result of either the family of chemical reactions that are inherent to the pure mixture and the effect of heat in accelerating such reactions, or by a variety of impurities that readily react with propellant components. Ions capable of existence in solution in more than one oxidation state, ions capable of cyclic oxidation-reduction, and species that readily form coordination complexes are examples of the sorts of material that, if present as impurities, would be expected to alter the thermal stability of these mixtures significantly. The inherent thermal

stability of the pure propellant is not necessarily the same as that of the mixture once it has begun to thermally degrade. Accelerated decomposition, commonly called thermal aging, has been observed in many chemical systems and could reasonably be expected to occur in the HAN-based liquid propellants. In addition, chemical species that react with the transient ions and free radicals that are produced during combustion can be expected to influence the performance of the propellants although they may not affect storage stability. Evaluation of the thermal stability of the propellants and of the effects of impurities and contaminants on both storage stability and efficacy are therefore major topics in the overall development of liquid propellant weapon systems. Since the propellants are quite different, both physically and chemically, from solid propellant mixtures that have been used heretofore, it would seem reasonable to expect that stability criteria and the methods and considerations needed to arrive at such criteria will be different also.

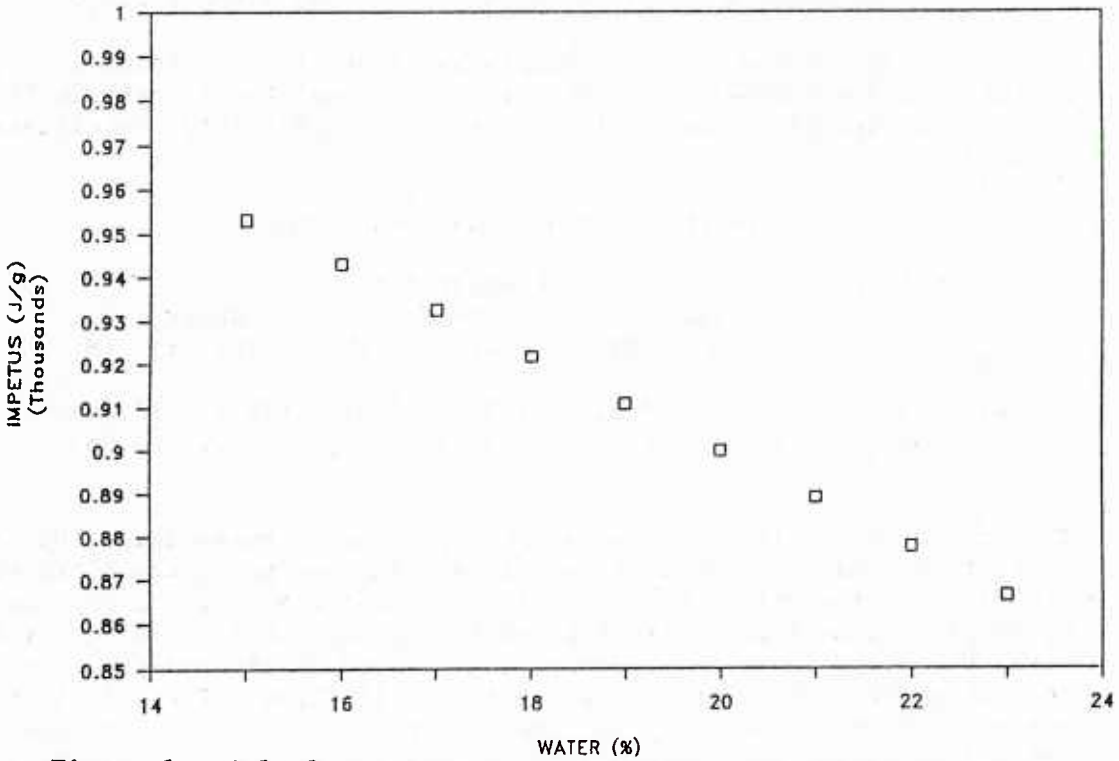

Figure 1. Calculated Impetus as a Function of Water Content

2. THERMAL STABILITY

Thermal stability, the principal subject of this report, can be defined precisely as the absence of <u>any</u> change in the material under investigation after exposure to a specific thermal routine. This definition is of limited practical value because a guideline for propellant stability must address safety and efficacy after storage rather than purity or constancy of physical properties. A stability guideline is also needed in order to prepare production specifications.

The climatic conditions under which Army materiel will be stored and under which they are expected to operate are described in Army Regulation No. 70-38.[4] The worldwide temperature extremes cited in the Regulation range from one hour at 71°C to continuous storage at -51°C. Since no geographical restriction is to be placed on liquid propellant gun systems, the climatic extremes form the basis for development of storage stability specifications and for the design of tests that assure that such specifications are met.

The water content of the HAN-based propellants creates an almost unique situation that impacts on thermal stability considerations and can have severe consequences if not addressed properly. As seen in Table 1, the propellants LGP1845 and LGP1846 contain 16.8 and 20.0 % water respectively. The vapor pressure of the propellants is essentially the vapor pressure of their water component and the chemical composition of the vapor is pure water.[5] If propellant is stored in such manner that the gas space above the liquid is in equilibrium with its surroundings, water will be gained or lost depending on environmental temperature and relative humidity. Compositional integrity of the propellants would thus be lost and both storage stability and efficacy strongly affected. It is therefore mandatory that any production and storage specifications for the propellant include its container and that the container be designed such that the propellant be isolated from its environment. The container, of course, also serves as the means to prevent contamination of the propellant during its service lifetime. The matter of post-production contamination is related to, but separate from, thermal stability and will not be directly addressed herein.

A reasonable value for propellant storage life is 20 years. This requirement poses a severe problem for the laboratory investigator who usually is faced with time constraints that do not permit such extended studies. Techniques must therefore be devised that will produce experimental data quickly and that are suitable for extrapolation. This last point is, by no means, trivial since many of the experimental methods that have been used in the past and are collectively referred to as "accelerated storage testing" do not possess the scientific foundation to permit extrapolation. Requirements for the validity of accelerated storage testing data as a prediction of storage life are that reaction mechanism does not change with changes in temperature over the range under consideration, i.e.. (a) that <u>all</u> of the reactions observed also take place under the more benign conditions of operational storage and (b) that the change in reaction kinetics with temperature be known.

Generally, the rate of reaction of a chemical compound is expressed by:

$$- dC/dt = kC^n \qquad (2)$$

where k is the reaction rate constant,
C is the reactant concentration,
and n is the reaction order. If the rate constant can be described by the classical Arrhenius equation:

$$k = A \exp(-E_a/RT) \quad (3)$$

where A is the frequency factor,
E_a is the activation energy,
R is the universal gas constant,
and T is temperature, then knowledge of the values of A and E_a permits extrapolation of reaction rates to other temperatures. As a rule, propellant decomposition is chemically complex and involves a number of reactions that take place simultaneously. The products of these reactions often react with the propellant and with one another and the observed reactions are the sum of a number of simpler reactions. The reaction rates determined from such observations produce what is commonly termed "global" kinetics which may or may not follow the simple Arrhenius rate expression. In either case, one cannot determine *a priori* whether temperature extrapolation of the data is valid. The role of impurities greatly complicates these considerations since their presence usually introduces new families of reactions that bring with them their own reaction kinetics. The effect of these impurity reactions are not necessarily additive.

Although an absolute measure of thermal stability is faced with the difficulties cited above, the relative effect of variation in component concentration or of impurities or contaminants can be more readily determined. Such measurements produce a ranking that is relative to the thermal stability of an arbitrarily defined "pure material" and are often of substantial value. If thermal stability studies are to address these latter considerations, the test methods employed can also become somewhat empirical in that they should produce data that are related in a straightforward manner to the thermal stability of the propellant without actually measuring the rate of disappearance of one or more of the component compounds.

A second requirement that is frequently placed on accelerated aging tests of propellant stability is that the samples used for testing be much smaller than the propellant packages actually in storage. Although the need for such a requirement is intuitively obvious, one consequence can lead to serious errors in storage lifetime prediction. Small samples attenuate the effect of sample self-heating that is the result of slow, exothermic reaction because heat transfer from sample to surroundings is more efficient for a small sample. Since reaction rates increase when temperature is raised, the effects of self-heating are amplified as some function of sample size. Failure to take this effect into account could result in serious overestimation of the thermal stability of the material being evaluated.

II. BACKGROUND

Much of the early work that is applicable to thermal stability assessment was not carried out for that purpose but rather had propellant characterization as a goal. Such matters as the nature of the reaction sequence, the intermediate reaction products, and parametric studies involving the controllable variables had not yet been investigated and required attention. Information applicable to the thermal stability of the propellant mixtures was, in many cases, obtained incidentally to the main objective of the experiments.

1. THE AMINCO BOMB

One of the first liquid propellant characterization test methods devised was a thermal reaction initiation scheme that produced data that is related to the thermal stability of the mixtures and their components. A laboratory-scale, high pressure hydrogenation system, manufactured by the American Instrument Company (AMINCO), was used for these studies. The system consists of a 50 mL capacity sample chamber, furnace, and associated tubing and valves for pressurizing and venting. The sample chamber was made of passivated ANSI 316 steel and had a safe-pressure rating of 96.5 MPa which limits propellant sample size to 1-2 mL. Since the HAN-based propellants are ionic and slightly acidic, containing both oxidizing and reducing species, they are highly corrosive. Although brasses, carbon steels, and most aluminum alloys cannot be used in components that will come in contact with these propellants and their decomposition products if reproducible results are to be obtained, a number of stainless steels, after proper passivation, are usable.

The furnace assembly is designed to heat the chamber and its contents uniformly and is calibrated by recording the output of a thermocouple mounted inside the sample chamber as a function of time at a given heating rate. The furnace heating rate settings produce highly reproducible heating rates and reaction onset temperature is determined from these calibrations since internal temperature cannot be measured if pressure data are to be taken. If a heating rate of 4-5^{o}C/min is used, the propellant undergoes reaction within 30 minutes of the onset of heating. The pressure vessel is equipped with an interchangeable fitting that permits use of either the thermocouple or a pressure transducer and a sampling port. In use, the chamber is filled, sealed, placed in its surrounding furnace assembly, and purged with nitrogen or helium before commencement of the heating cycle. Reaction initiation is usually detected by an increase in pressure in the chamber. The experimental data obtained with this apparatus are P_{max}, the maximum pressure obtained, the shape of the curve from reaction initiation until P_{max}, and the temperature at which the pressure excursion begins, T_i.

If ignition and combustion of the samples is to follow thermal initiation, pressurization of the chamber is usually required. Such pressurization can be self-generated, the result of early thermal decomposition if the sample is large enough, but is most easily achieved

by charging the vessel with nitrogen or helium prior to commencement of the heating cycle. Such prepressurization has a small but measurable effect on reaction initiation temperature.[6] The tendency of the liquid to produce droplets that are thrown from the region of reaction resulting in an extended reaction zone is probably a major contributor to the pressure sensitivity observed. Values of P_{max} are closely related to the impetus of the propellant whereas the shape of the pressure-time curve is strongly dependent on the kinetics of ignition and combustion. Values of T_i are related to the chemical equilibria that exist in the propellant mixtures and are often quite sensitive to the presence of impurities.

The AMINCO bomb has produced a variety of data in addition to the pressure dependence already noted. It was found that initiation temperature of propellant mixtures that were free of contaminants or impurities was dependent solely on the total nitrate ion concentration of the mixture[7] indicating that reaction of the nitrate ion initiates the ignition process. The piezoelectric pressure transducer is fast enough to produce data related to the ignition and combustion processes taking place within the chamber and such data has been used to show the effect of molecular structure of the fuel component on the rate of combustion.[8] Sampling of gaseous and liquid reaction products[9] has also led to explanation of some of the combustion reaction pathways. The effects of certain contaminants and additives on both P_{max}, and T_i have been documented.[10] Recently, the effect of oxidizer-to-fuel ratio was studied[2] and confirmed the validity of thermochemical calculations using the BLAKE code.

The thermal initiation testing method described produces a furnace generated temperature ramp that is totally independent of reactions taking place in the sample. Since the pressure transducer is connected to a charge amplifier operating in a capacitive mode, thermal initiation data are obtained only in cases where initiation results in gas production at a rate that is high enough to produce a measurable output from the charge amplifier. An example of this limitation was observed when mixtures of HAN and hydroxylammonium formate were permitted to react.[11] The rate of gas production is so slow for these mixtures that no record indicating that reaction had taken place was obtained until gas sampling and static pressure measurements at the completion of the heating cycle indicated that the mixtures had reacted completely.

The programmed temperature ramp obtained with the AMINCO bomb resembles the experimental conditions available with differential scanning calorimeters (DSC), although the data obtained are quite different since, in the case of DSC, a thermal history of the sample is obtained. Attempts have been made to use DSC data for HAN-based propellant stability screening.[12-13] Unfortunately, the gas and droplet production that is characteristic of reaction initiation in these materials causes such extensive scatter in the data that the techniques employed seem of limited value.

Thermal reaction assessment techniques that rely on temperature ramp heating of the sample all suffer from the same deficiency, namely, that the effect of slow exothermic reactions are suppressed. This effect is supplementary to a similar shortcoming associated with the use of small samples. These limitations have been discussed in some detail[14] and have led to the development and use of adiabatic calorimeters for the evaluation of thermal hazards in chemical systems. Such calorimeters, when used properly, produce data that are independent of sample size and can provide both thermodynamic and kinetic data for chemical systems that react slowly. Unfortunately, no commercially available system is fast enough to accurately acquire the kinetics data associated with propellant ignition and/or combustion. An accelerating rate calorimeter (ARC), produced by Columbia Scientific Instruments Corp., Austin, TX, has been modified so that it possesses all of the capabilities of the AMINCO bomb in addition to its inherent functions. Since both reaction initiation temperatures and the nature of the reactions that take place when reaction is initiated are required for proper thermal stability assessment, the principles of operation of the ARC and its application to the study of liquid propellants will be described in subsequent sections.

It should be remembered that the purpose of propellant storage testing is to determine the effect of thermal stress, contaminants, and impurities on propellant safety and efficacy. An example of a group of impurities that has little or no effect on the thermal stability of the HAN-based propellants are the halides of the alkali metals, sodium chloride being the most common.[9] Examination of the data reveals that while the presence of chloride ion has virtually no effect on reaction initiation temperature, it strongly suppresses combustion and, at concentrations as low as 35 millimolar (40 ppm), combustion is totally inhibited. The example emphasizes the limitations of simple "go-no go" thermal stability tests and suggests that such tests should not be used unless the reactions of the chemical system are sufficiently understood to assure the validity and implications of the test results.

2. OTHER DATA

One study that specifically addressed the role of impurities on the thermal stability of the HAN-based propellants was an investigation of the mechanism and kinetics of the reactions of propellant with ions of the transition metals copper and iron.[15] These studies were carried out using classical laboratory techniques for investigation of homogeneous reactions in solution. It was found that the AAN salt played no role in the reactions observed, the metal ions reacting only with the HAN that was present. Although the stoichiometry of the reaction is the same for both metals, namely metal:HAN = 2, the reaction of HAN with Cu^{2+} follows a second order rate law, first order in HAN and in Cu^{2+}, whereas the reaction of HAN with Fe^{3+} follows a third order rate law, first order in HAN and second order in Fe^{3+}. In addition, the composition of the gases that are products of these reactions are different, the Cu^{2+} products being N_2O and N_2 while the Fe^{3+} product is exclusively N_2O. Cu^{2+} concentration decreases as the reaction proceeds but Fe^{3+} remains

constant, indicating that Fe^{3+} catalyses the HAN decomposition but Cu^{2+} does not. Values of A and E_a were obtained for both reactions and since reaction mechanism does not change over the temperature range 25 to 85°C, these values can be used for prediction of the thermal stability of propellant containing Cu^{2+} and/or Fe^{3+} as impurities. Quite obviously, the reaction mechanisms observed are different for the two metal ions investigated and serve to reinforce the caveats presented in the previous Chapter.

Thermal stability investigations of the HAN-based propellants and their components have been undertaken at various laboratories. A number of qualitative or semi-quantitative studies indicate that the propellant becomes less thermally stable after exposure to various materials. Such observations, some of which were undertaken to determine the compatibility of propellant and the materials, could serve as a starting point for thermal stability studies but do not contribute significantly to an understanding of the thermal deterioration of the propellants.

Thermal stability studies are presently under way[16] at the Royal Armament Research and Development Establishment (RARDE), Waltham Abbey, UK. An LKB* Model 2277 microcalorimeter has been used and an ARC** has recently been acquired and is now in use for these investigations. Propellant samples containing dissolved salts of iron, copper, cobalt, nickel, and several other metals are being examined but no more than preliminary data are available at this time. Although the two calorimeters are fundamentally different in both design and capability, they each are able to produce data that should be widely applicable.

A second technique under investigation at RARDE employed thermogravimetry. A Mettler*** Model TG50 thermobalance was used and the temperature at which half the original sample weight is lost recorded. The addition of copper and iron salts to propellant causes the measurement criterion to be achieved at lower temperatures indicating that the presence of such impurities results in decreased thermal stability. A method for quantitative comparison of these data with results obtained via calorimetry does not appear to exist at this time.

A series of thermal stability investigations were carried out using LGP1846 containing a variety of metal ions at the Fraunhofer Institute for Chemical Technology (ICT) under US Army Contract DAJA 45-86-C-0056. These experiments were conducted at 90°C although no attempt was made to demonstrate that the data obtained were applicable to lower temperatures. Gas evolution was monitored as a function of time and propellant samples were analyzed after storage although the gases produced were not. The extent to which these data relate to thermal stability is not known although some qualitative correlation appears evident. Of the 23 metals investigated, the rate of gas production was highest for samples

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*LKB Biochrom Ltd, Cambridge, England
**Columbia Scientific Instruments Corp., Austin, TX,
***Mettler Instruments Ltd, High Wycombe, England

to which V^{4+} had been added although the change in composition of the propellant was smaller than in samples to which Cu^{2+} or Fe^{3+} had been added. One can only assume that the molecular weight of the gases produced in the samples containing V^{4+} was lower than in those containing Cu^{2+} or Fe^{3+}, a supposition that implies that hydrogen may be a significant reaction product. Hydrogen, in small quantities, had been obtained as a reaction product in HAN-fuel mixtures that are fuel rich but has not been observed in stoichiometric mixtures such as LGP1845 or LGP1846. If the V^{4+} containing samples produce hydrogen, it will be the first instance in which hydrogen was obtained from the decomposition of these propellants and would indicate that the presence of V^{4+} causes major changes in the propellant decomposition reaction mechanism.

III. EXPERIMENTAL METHODS

The experimental approach selected at this Laboratory for thermal stability testing of the HAN-based liquid propellants was adiabatic calorimetry since it was felt that the evaluation of thermal stability using this technique would produce data that are most readily amenable to extrapolation to conditions of practical importance. Although adiabatic calorimetry is in principle very simple, the design of a functioning instrument requires consideration of some relatively complex concepts.

1. THE ACCELERATING RATE CALORIMETER

In a chemical reaction that obeys Arrhenius rate laws, the rate of an exothermic reaction will increase if the temperature or concentration of reactant is increased. If the system is well insulated so that heat is not readily removed, the temperature of the system and hence its reaction rate will increase as the reaction progresses. The rate will continue to increase until enough reactant has been expended to significantly lower its concentration. There are numerous examples of accelerating reaction rates under near adiabatic conditions, one of which is bulk storage of some almost pure chemical that undergoes slow thermal decomposition. At early times, the concentration of reactant is high and the small changes in concentration caused by the early stages of reaction are insignificant. The large quantity of reactant being stored prevents heat from being readily removed and an exothermic reaction thus results in an exponentially increasing reaction rate that leads, in many cases, to runaway conditions with heat and reaction products being evolved in amounts that exceed the yield strength of the container in which the material is stored. This almost assuredly will be the case with energetic materials since energy content is high and reaction rates, and hence energy release rates, are rapid. Thus, thermal reaction measurements under adiabatic conditions would provide worst-case, and therefore, most conservative circumstances.

a. Operating Principles The ARC consists of a very well insulated chamber containing several heating elements, that holds a small sample container. The sample container is usually a spherical bomblet, 2.5 cm

in diameter, with a length of tubing, 3 mm in diameter and approximately 3 cm long, attached. The tube serves as sample inlet and provides a means for connection of the bomblet to the rest of the apparatus. The bomblets are fabricated by electron-beam welding in order to avoid contamination. A sensitive Nicrosil-Nisil thermocouple (type N), attached to the sample container, monitors the evolution of heat from the sample and thus detects the onset of exothermic reaction. If heat production is detected, the chamber heaters are activated and attempt to minimize any temperature difference between the sample and the chamber, thus eliminating heat transfer from the sample container and creating the equivalent of adiabatic conditions. A drawing of the essential components of the calorimeter is presented in Figure 2.

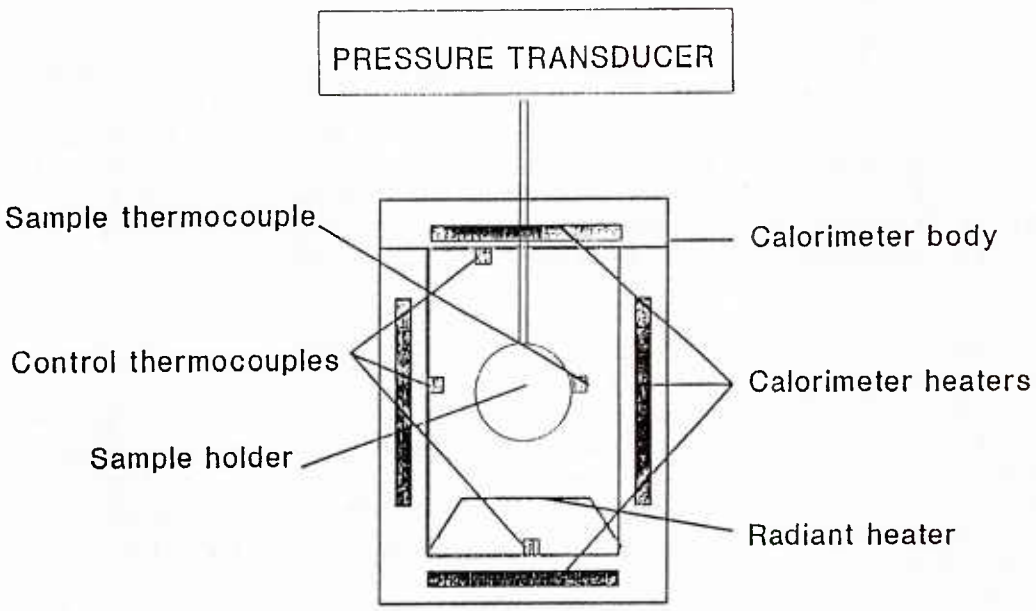

Figure 2. ARC Calorimeter Assembly

Calibration of the instrument establishes the amount of electrical power required to achieve and maintain a given temperature under conditions that closely approximate those found when samples are tested. These data, stored in the ARC computer memory, are compared with data obtained when a sample is present. Thus, the difference in electrical power used by the heaters as a function of time and temperature readily translates into the heat evolved by the sample as it reacts. In cases where the rate of heat evolution from the sample is less than the maximum heating rate of the chamber, a variety of thermodynamic and kinetic data become available for evaluation.

In order to produce an instrument of practical value, the heaters are programmed so that the chamber (and sample) are heated to some preset temperature and then held at that temperature for a predetermined

time. During that time the output of the thermocouple is monitored. If no heat production is detected, the chamber is heated to a higher temperature and the sequence repeated until the maximum programmed temperature is obtained. Since the mass and heat capacity of the sample container is known, the amount of heat necessary to produce a change in temperature is readily determined and is one of the criteria for sample size selection. Thermocouple response, typically 0.01°C, determines the accuracy and error band of the measurement. Prudent selection of operating parameters results in data that are independent of sample size and can therefore be extrapolated to large samples. The data obtained can provide values of E_a and k (equation 3) and will predict conservative safe storage temperatures for both the pure material and for material containing impurities or contaminants.

The response time of the thermocouple and the data sampling rate of the ARC electronics, 100 data points per minute, limit its applicability to reactions that evolve heat at a slow to moderate rate. The maximum output of the heating elements in the calorimeter, approximately 10°C/min, also serves to limit its applicability since adiabatic conditions require that the temperature difference between sample and chamber be minimal. Although adequate for most thermal stability evaluations, the data sampling and heating rates are far removed from the rates that would be required to accurately track a rapidly burning propellant so that the ARC, as delivered, cannot produce either the thermodynamic or kinetic data associated with propellant ignition and combustion.

b. Equipment Design The ARC is able to provide a great deal of information in addition to safe storage temperature. Several additions and small modifications made available all of the capabilities of the AMINCO bomb and thus further enhanced its usefulness. One of the first considerations for use of the ARC for HAN-based propellant evaluation was selection of a proper sample container. Although passivated ANSI 316 stainless steel had been successfully used in the past, sample bomblets made of this alloy gave results that were not reproducible. Inspection of the inside of a used bomblet revealed the presence of rust and corrosion in the vicinity of the electron-beam welds used to join the hemispheres and the filling tube. Apparently, the welding process changed the composition and/or structure of the alloy enough to make it unusable. It was decided, based on this experience, to select a pure metal rather than an alloy for the sample bomblet. Yield strength and heat capacity, in addition to lack of reactivity, were factors that influenced selection. Tantalum had been shown[17] to be unreactive to the HAN-based propellants and their decomposition products and bomblets with 0.76 mm thick walls of 2.5 and 1.3 cm diameter were fabricated. Safe operating pressure of the 2.5 cm container is 14 MPa and safe pressure using a 1.3 cm container of the same wall thickness should be 55 MPa, a value that exceeds the limitations of other ARC components. The heat capacity of tantalum is 0.0334 cal g^{-1} K^{-1} [18] and the 1.3 cm bomblet typically has a mass of 8 g. The volume contained by the 2.5 cm bomblet is 8.6 mL whereas the 1.3 cm bomblet has a volume of 1.1 mL. Sample loading densities of 0.03-0.06 g/mL, the values used in the AMINCO bomb,

are obtained with 0.02-0.04 mL samples in the 1.3 cm bomblet. The smaller diameter bomblets*, because of their smaller mass and volume, and higher yield strength, are the containers of choice and have proven to be completely satisfactory. The bomblet is joined to the ARC via a tube fitting and care is required to assure that this fitting remains gas tight during the entire experimental cycle. The difference in properties between tantalum and the ARC fitting to which the bomblet is joined mandates that tantalum ferrules be used at this connection.

The 600 ms/point ARC data sampling rate, while quite adequate for assessment of thermal stability, is not able to follow the rapid reaction sequences that occur once reaction in the propellant sample is initiated. Temperature response is limited both by thermocouple response time and by thermal inertia due to the mass of the sample bomblet. Thermocouple response time is considerably faster than the data sampling rate of the system and faster data sampling and recording was accomplished by tapping the Type N bomb thermocouple output and routing it to a Newport** Model 70 differential amplifier, the output of which is sent to one channel of the Model 4562 Amplifier of a Nicolet*** Model 4094 Digital Storage Oscilloscope, sampling at the rate of 5 ms/point. A Datel**** Model DVC 8500 voltage calibration source is included in the ungrounded side of the thermocouple output so that the voltage recorded by the oscilloscope can be accurately converted to temperature. Oscilloscope impedance is high enough that the thermocouple signal is not degraded, an important consideration since operation of the ARC was not to be adversely affected by any of the modifications that were to be made.

A second channel of the oscilloscope amplifier recorded the output of a Kistler***** Model 5004 Charge Amplifier to which was connected a Model 601b pressure transducer so that the pressure-time history of the combustion event, recorded at the same rate as the thermocouple output, was also obtained. The charge amplifier output was also routed to a second Model 4562 Amplifier operating at 0.05 ms/point since response of the pressure transducer is fast enough to show the combustion event in considerable detail. The ARC contains an RS-232 I/O board permitting transfer of data to an appropriate device, in this case, an AST****** Model 286 personal computer. The data collected and stored by the oscilloscope can be transferred to the same computer and subsequently processed. Thus, files are created containing all of the information produced in a given experiment. A block diagram of the calorimeter showing the modifications is presented in Figure 3.

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* fabricated by Midland Corrosion Materials, Howell, MI.
** Newport Electronics, Inc, Santa Ana, CA
*** Nicolet Instrument Corp, Madison, WI
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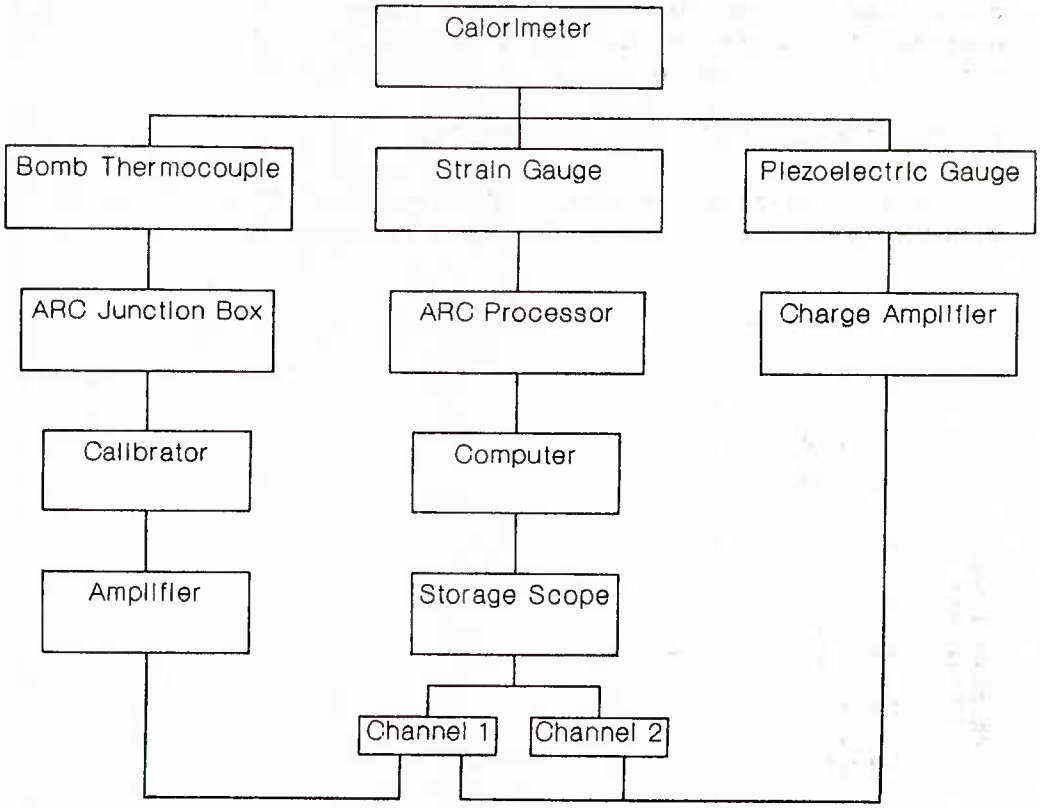

Figure 3. Calorimeter Arranged for Fast Temperature and Pressure Recording

2. OTHER TEST METHODS

The test methods in use at RARDE and ICT were briefly discussed earlier. Concomitant with any test method in which propellant reactions are being monitored must be a set of rigorous analytical procedures that provide the information that will be used in treatment of the data. In this regard, the methods developed for propellant and reaction product analysis at ICT[19] are noteworthy. The procedures reported are all based on titrimetry and can be used in a variety of situations. They cover both propellant assay and the determination of impurities or reaction products.

IV. RESULTS AND DISCUSSION

Although the purpose of this report is to describe thermal stability testing of the HAN-based liquid propellants in general, and thermally induced reactions and the applicability of the ARC for obtaining such data in particular, some of the results obtained serve to illustrate the capabilities and versatility of the equipment. When studied at atmospheric pressure, thermal decomposition of the

propellant, rather than ignition and combustion, is seen. Aqueous samples of HAN and/or TEAN are incapable of combustion and thus produce data similar to that obtained with unpressurized propellant.

1. THE ACCELERATING RATE CALORIMETER

A typical pressure trace, obtained with 30 μL of LGP1846 at a nitrogen pressure of 2 MPa, is shown in Figure 4.

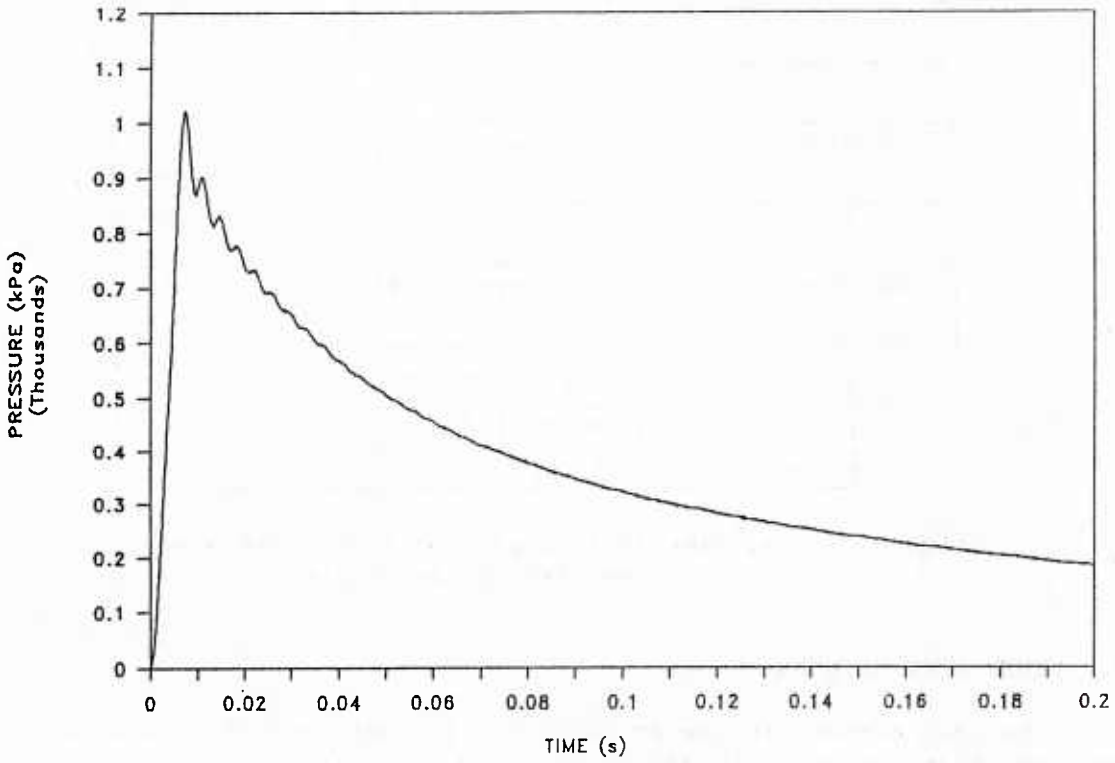

Figure 4. Pressure-Time History of the Reaction of LGP1846 in an ARC Bomblet

A maximum pressure of 1.02 MPa is seen 7.3 ms after reaction commences and a regular oscillation at a frequency of 250 Hz is also apparent. The origin of the oscillation is an acoustic resonance produced in the tubing that connects the bomblet to the piezoelectric pressure transducer and is seen in virtually every pressure record obtained. Frequency is dependent on length and diameter of the tubing used and the oscillation is readily removed by filtering the data with a digital, narrow-band, rejection filter. A maximum is seen in the Figure 4 data because pressure is affected by the thermal inertia of the bomblet. Since the gas that is rapidly evolved is at a much higher temperature than the sample container and cools by heat transfer to its walls, the rate of decay of pressure is smooth and monotonic. Gas and heat evolution is probably completed by the time the pressure maximum is seen

since the pressure decay, caused by contraction due to cooling, is fitted very well by a logarithmic function. The maximum pressure recorded will be less than the peak pressure because gas and heat production, although very rapid, is not instantaneous. Extrapolation of the logarithmic cooling curve should result in a value of the maximum pressure that is free of the effect of heat transfer during reaction. An uncertainty is introduced by such extrapolation due to the selection of a proper value of time.

The effect of processing using a digital filter, 28 Hz wide centered at 250 Hz, and the fit of the pressure data obtained between 10 and 175 ms to the function:

$$P(t) = A + B*\ln (t-t_o) \qquad (4)$$

where $A = -260.2$,
$B = -255.0$,
and $t_o = 0$ are shown in Figure 5.

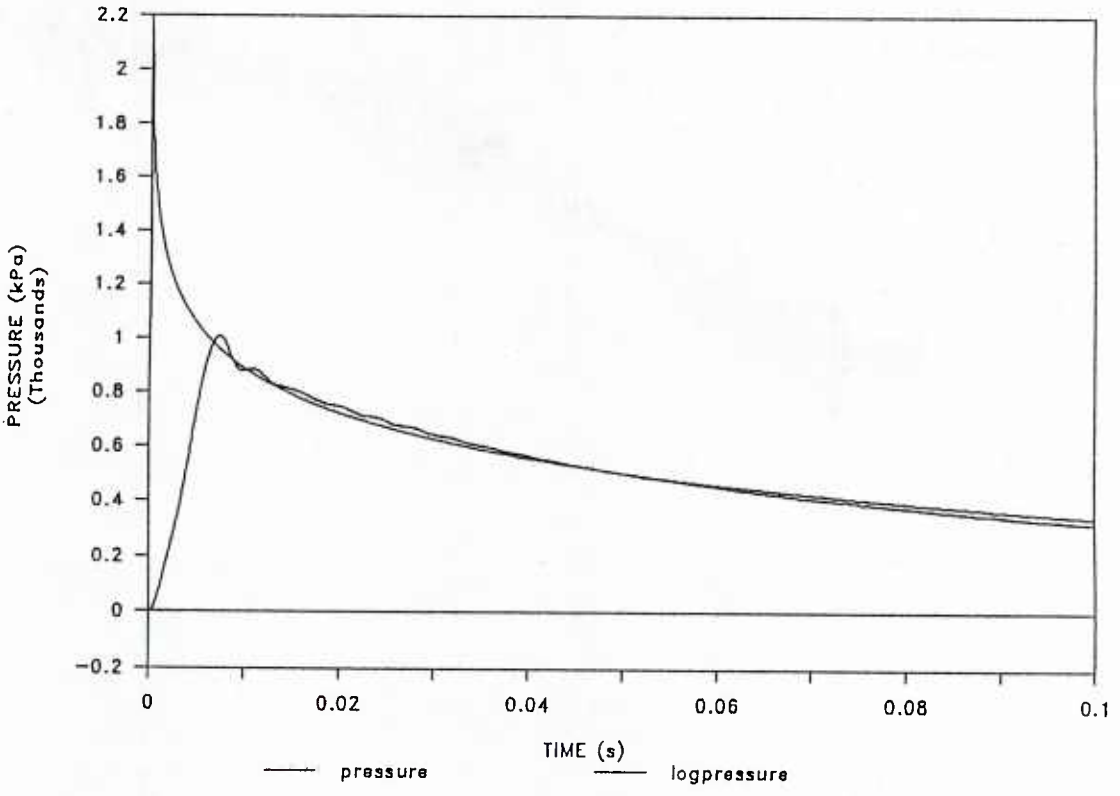

Figure 5. Filtered and Extrapolated Pressure History of the Reaction of LGP1846

The maximum pressure obtained using the filtered data is 1.01 MPa at 7.3 ms and is in excellent agreement with the unfiltered results thus indicating that the filtering procedure does not produce significant degradation. Calculation of peak pressure under these experimental conditions using the BLAKE thermochemical code[3] results in a value of 2.29 MPa and extrapolation of the fitted cooling curve results in a value of 2.24 MPa at t = 0. The fairly good agreement between extrapolated and calculated values of maximum pressure has practical value because it indicates smooth and complete combustion. It is not obtained when combustion is incomplete or when a slight hesitation in gas generation is observed although the sample is consumed completely. The significance and validity of selecting extrapolation to t = 0 will not be discussed in this report.

The thermocouple response obtained simultaneously with the Figure 4 data is shown in Figure 6.

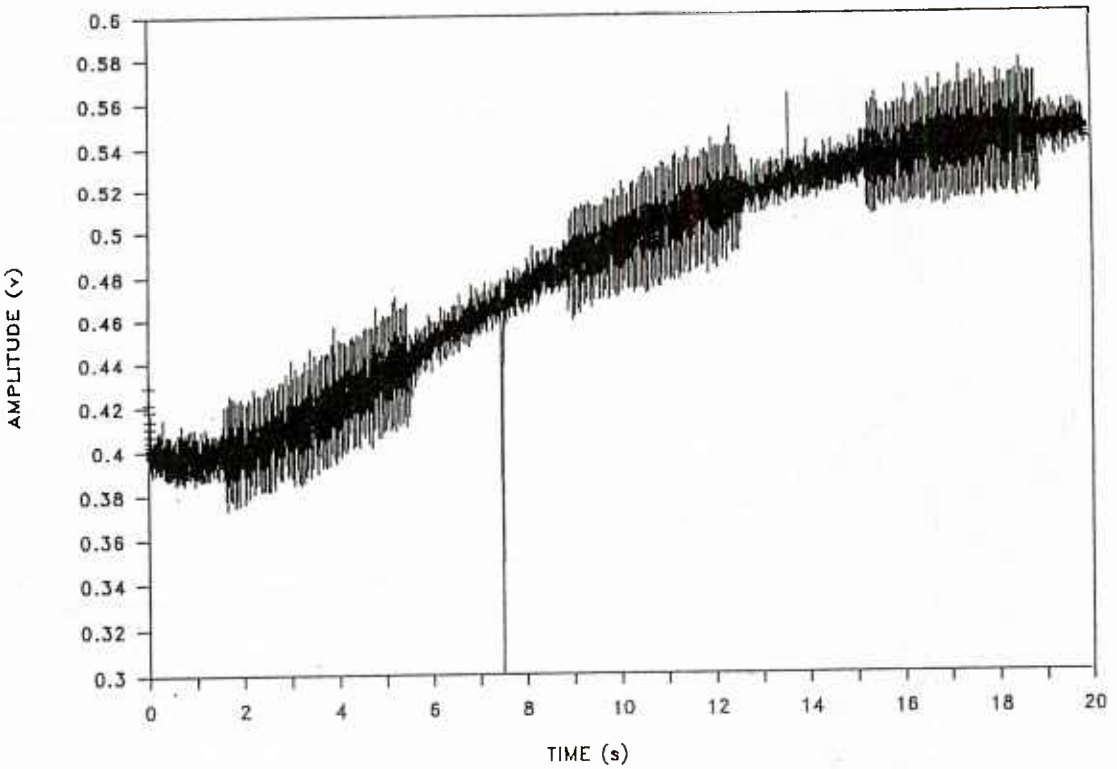

Figure 6. Thermocouple Response to Reaction of LGP1846 in an ARC Bomblet

The noise signal prominent in the data is removed using a 25 Hz low pass filter, the results appearing in Figure 7.

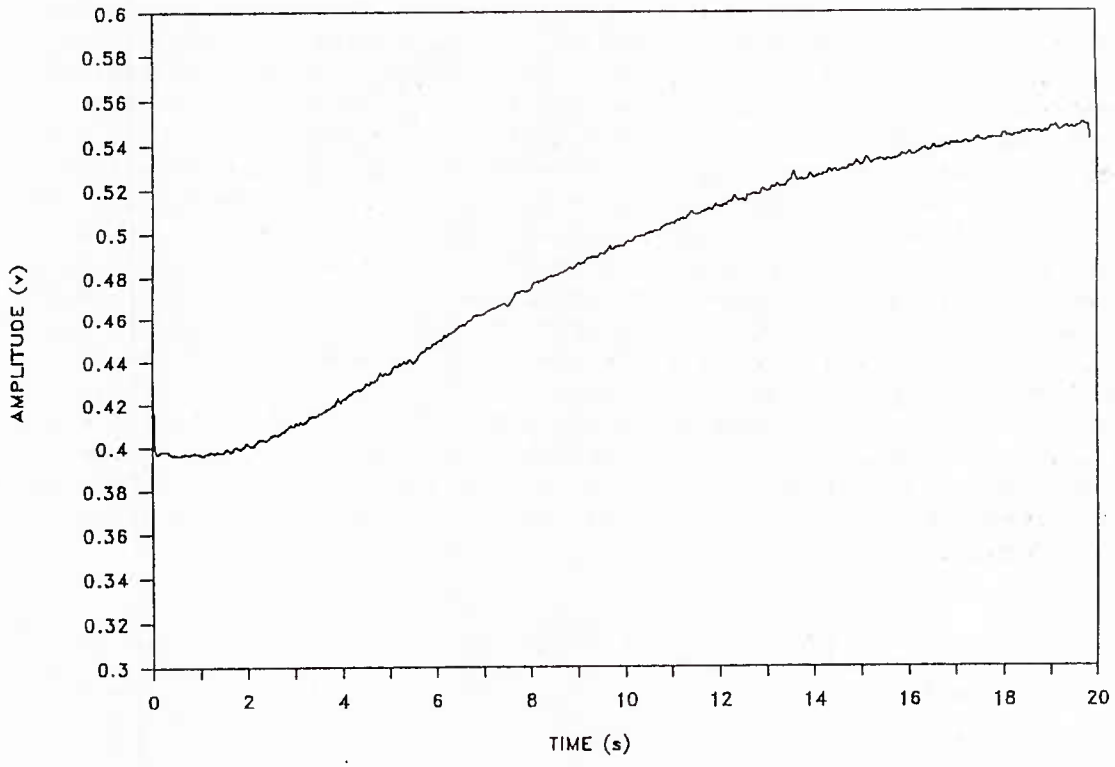

Figure 7. Thermocouple Response Data After Filtration

The filtered data are then processed by incorporating amplifier gain and temperature response of the type N thermocouple to produce the temperature-time history shown in Figure 8. The time scale needed to obtain a temperature history of an exothermic event is slower than that required to obtain the associated pressure history because the mass of the bomblet limits the speed of the system. In fact, the temperature measured at the outer wall of the bomblet at the time that maximum pressure is obtained indicates no significant heat transfer and adds to the validity of the pressure extrapolation shown in Figure 5. The temperature and pressure data routinely published by the calorimeter indicate that the pressure excursion shown in Figure 4 took place when bomblet temperature was 122°C. It is noteworthy that the ARC detected the onset of exothermic activity 18° below the temperature at which the pressure excursion is seen. No maximum is seen in Figure 8 because the calorimeter heater circuits had engaged before the trace was completed and were attempting to raise calorimeter temperature in order to minimize any difference between the bomblet and the calorimeter body. The rate of temperature change observed during the more active part of the excursion substantially exceeds the 10°/min maximum heating rate of the calorimeter and attempts at kinetic analysis of the thermal data will not be valid. The Figure 8 data seem to show a rapid heating rate at the early portion of the curve followed by heating at a slower rate. The data record produced by the calorimeter shows that the temperature rise associated with the exothermic event recorded in Figures 4 and 6 was 36°C whereas the portion recorded in Figure 8 shows a rise of 26°.

The discrepancy, combined with the observation that the Figure 6 data still has a positive slope at the end of the record, indicates that the oscilloscope record is incomplete. The inability of the calorimeter heaters to maintain adiabatic conditions during the event makes it probable that the value obtained from the calorimeter record is lower than the "true" value. The magnitude of this deviation from adiabatic conditions is seen by assuming that the error incurred is small. The heat needed to raise the temperature of the 8.0198 g bomblet 36° is 40.3 J. The propellant sample, with a mass of 0.0449 g, results in a loading density of 0.04 g/mL for which the energy released by combustion of LGP1846 is 4364.1 J/g. The energy expended in raising the temperature of the bomblet accounts for 898.1 J/g, a mere 21 % of the available energy. Although the deviation from adiabaticity produces a substantial error, it does not account for 79 % of the available energy because the energy released by combustion of the sample is expended by a number of processes in addition to raising the temperature of the sample container. Discussion of these processes is well beyond the scope of this report.

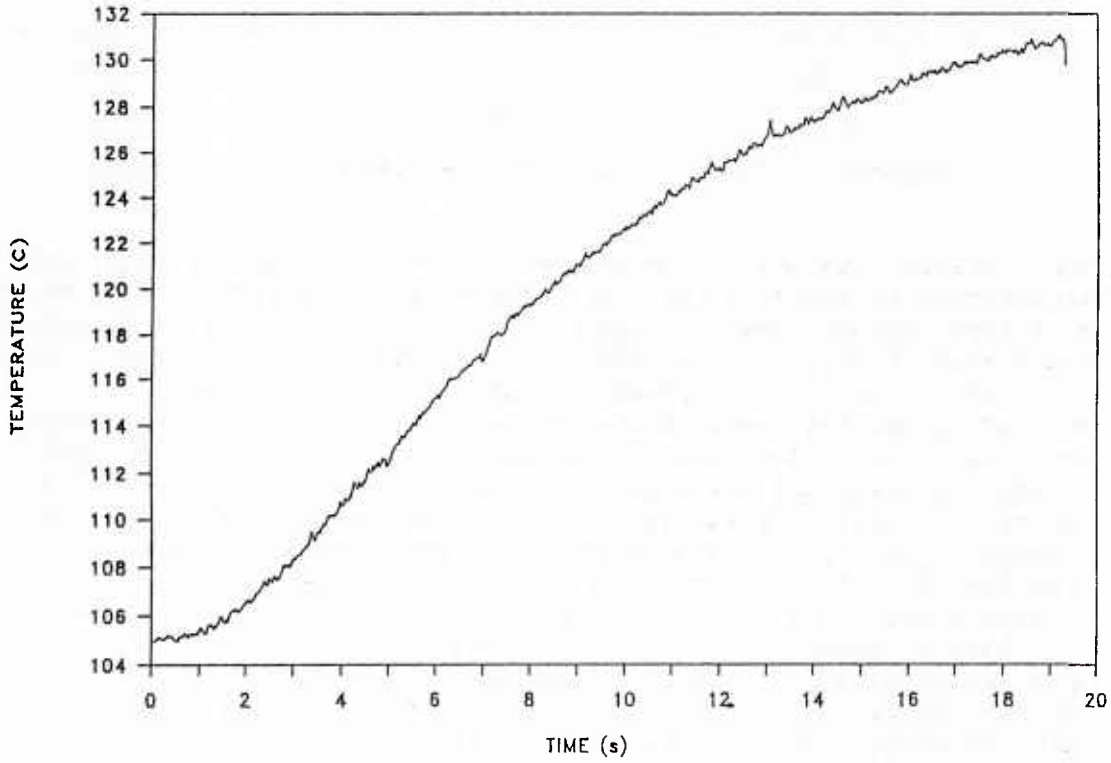

Figure 8. Temperature-Time History of the Reaction of LGP1846 in an ARC Bomblet

2. OTHER DATA

The ARC without modifications or additions produces data that are of considerable value in developing an understanding of the thermal reactions of the HAN-based propellants. Samples of 20-30 mg of LGP1846 that are not pressurized produce exothermic sequences at 122, 180, and 227°C. Samples of 10.4 molar HAN produce exothermic sequences at 122 and 180°C and TEAN samples exhibit exotherms at 180 and 227°C, the specific HAN concentration having been selected so that nitrate ion concentration is the same as it is in the propellant. Samples of nitric acid also produce the 180° exotherm. The data available suggest that the exothermic reactions observed are the decomposition of the hydroxylammonium ion at 122°, the decomposition of nitrate at 180°, and the partial decomposition of the triethanolammonium ion at 227°. TEAN decomposition is incomplete because a tarry residue is recovered from the bomblet when TEAN or unpressurized propellant is the reacting sample. If the propellant sample is pressurized, a vigorous reaction is seen only at 122°C and water is the only condensed product recovered after the bomblet is cooled.

Although quantitative data relevant to reaction kinetics are not yet available because not enough is known about the reaction mechanisms associated with the reactions being observed, the ARC data can be used to identify changes in reaction mechanism when the propellant is chemically modified. Changes in the pattern of the exotherms obtained are strong indicators of a change in reaction mechanism. Thus, if addition of a potential impurity results in exothermic sequences that are substantially different from those observed with pure propellant, one is safe in assuming that a new and different decomposition mechanism has been invoked. This is in marked contrast to the case in which addition of an impurity lowers the temperature at which the onset of exothermic reaction is seen but the exothermic pattern is essentially unchanged. In the latter case, the impurity has lowered the thermal stability of the propellant by lowering the value of E_a in equation (3) but the reactions that take place are the same and propellant efficacy may well be unaffected. In the case where reaction mechanism is altered, both storage stability and efficacy may be substantially affected and prediction of performance is virtually impossible other than to state that it will be different from that expected of pure propellant.

The calorimeter is currently being used to assess the effect of excess nitric acid on the stability and performance of propellant mixtures. In addition, studies of the effect of various ionic impurities in the parts per million concentration range are planned. Results of this work will be reported elsewhere.

V. CONCLUSIONS

The accelerating rate calorimeter is an excellent experimental device for the assessment of the thermal stability of liquid

propellants. The unmodified ARC provides kinetic and thermodynamic information applicable to thermal reaction initiation. In addition, the modified instrument produces data that apply to the ignition and combustion processes and thus greatly enhances the value of the system for propellant diagnostic studies.

Propellant stability and reactivity is influenced by various impurities and contaminants. These effects are often complex and although the overall consequence may be deleterious, producing a decrease in storage stability, the mode of interaction of the contaminant or impurity with the propellant can be quite different. The interaction of ions of the transition metals illustrate this point. In one case (Fe^{3+}) the metal ions catalyze decomposition, the reactions observed being essentially the same as those seen in uncatalyzed thermal decomposition. The impurity simply lowers the activation energy for reaction initiation. In other cases (eg. Cu^{2+}), the coordination complexes that are formed have markedly different physical and chemical properties than those of the ions normally present. These coordination complexes can, in addition to changing the storage stability of the propellant, effect the ignition and combustion characteristics and thus change the energy release rate. Still other cases exist where the presence of impurities (eg. NaCl) does not seem to impact storage stability but markedly suppresses combustion so that the efficacy of the propellant is compromised. It behooves those responsible for development of propellant specifications to be aware and understand these differences.

REFERENCES

1. Klein, N., Decker, M.M., Leveritt, C.S., and Wojciechowski, J.Q., "Low Temperature Calorimetry of HAN-Based Propellants," Proc. 23rd JANNAF Combustion Meeting, Vol III, p 133, 1986, CPIA Pub 457, Chemical Propulsion Information Agency, Laurel, MD.

2. Klein, N., Spiegel, C.A., and Messina, N.A., "The Effect of Oxidizer-to-Fuel Ratio Variation on Liquid Propellant Combustion," Proc. 1987 JANNAF Propulsion Meeting, Vol I, p 201, 1987, CPIA Pub 480, Chemical Propulsion Information Agency, Laurel, MD.

3. Freedman, E., personal communication.

4. "Research, Development, Test and Evaluation of Materiel for Extreme Climatic Conditions," AR 70-38, 1 Aug 1979, Department of the Army, Washington, DC.

5. Decker, M.M., Freedman, E., Klein, N., Leveritt, C.S., and Wojciechowski, J.Q., "HAN-based Liquid Gun Propellants: Physical Properties," BRL-TR-2864, Nov 1987, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

6. Klein, N., Sasse', R.A., Scott, R.L., and Travis, K.E., "Thermal Decomposition of Liquid Monopropellants," BRL Report No. 1970, Mar 1977, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

7. Klein, N. and Sasse', R.A., "Ignition Studies of Aqueous Monopropellants," ARBRL-TR-02232, Apr 1980, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

8. Klein, N., "Preparation and Characterization of Several Liquid Propellants," ARBRL-TR-02471, Feb 1983, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

9. Sasse', R.A. and Klein, N., "Thermal Initiation of Hydroxylammonium Nitrate Based Gun Propellants," Proc. 15th JANNAF Combustion Meeting, Vol I, p 313, 1979, CPIA Pub 297, Chemical Propulsion Information Agency, Laurel, MD.

10. Messina, N.A. and Klein, N., "Thermal Decomposition Studies of HAN-Based Liquid Monopropellants," Proc. 22nd JANNAF Combustion Meeting, Vol I, p 185, 1985, CPIA Pub 432, Chemical Propulsion Information Agency, Laurel, MD.

11. Klein, N. and Freedman, E., "A New Class of Improved Gun Propellants," Proc. 1984 JANNAF Propulsion Meeting, Vol II, p 287, 1984, CPIA Pub 390, Chemical Propulsion Information Agency, Laurel, MD.

12. Fifer, R.A., Decker, L.J., and Duff, P.J., "DSC Stability Test for Liquid Propellants," Proc. 22nd JANNAF Comb. Meeting, Vol II, p 203, 1985, CPIA Pub 432, Chemical Propulsion Information Agency, Laurel, MD.

13. Fifer, R.A. and Duff, P.J., "DSC Stability Test for Liquid Propellants: A Preliminary Report," BRL-TR-2837, Sep 1987, US Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD.

14. Townsend, D.L. and Tou, J.C., "Thermal Hazard Evaluation by an Accelerating Rate Calorimeter," Thermochimica Acta 37, 1-30, (1980)

15. Klein, N. and Wellman, C.R., "Reactions Involving the Thermal Stability of Aqueous Monopropellants," BRL Report No. 1876, May 1976, US Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

16. Bunyan, P., private communication.

17. Decker, M.M., Freedman, E., Klein, N., Leveritt, C.S., Wojciechowski, J.Q., Briles, O., and Joesten, L., "Compatibility Assessment of HAN-Based Propellants," Proc. 1987 JANNAF Prop, Char. Meet.- in press, Chemical Propulsion Information Agency, Laurel, MD.

18. "CRC Handbook of Chemistry and Physics," R.C. Weast, ed., CRC Press, Inc, Boca Raton, FL, p D-156, 1981.

19. Hansen, R., Backof, E., and De Greiff, H.J., 2nd Interim Report, Contract DAJA 45-88-C-0056, June 1987, Fraunhofer Institute for Chemical Technology (ICT), Pfinstal, FRG

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